US-PAT-NO: 5904523

DOCUMENT-IDENTIFIER: US 5904523 A

TITLE: Process for device fabrication in which a layer of oxynitride is formed
at low temperatures

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As observed by Saks et al., the NO species formed by the breakdown of N.sub.2 O
at the furnace temperature depletes nitrogen from the bulk of the oxide,
resulting in an unequal distribution of nitrogen in the oxide, with the bulk of
the nitrogen concentrated at the interface between the oxide and the underlying
substrate. Since nitrogen acts as a barrier to boron diffusion, the nitrogen
content at the oxide/substrate interface does not prevent boron from
penetrating the oxide, but, rather, merely prevents the boron from diffusing
further into the underlying substrate. The presence of boron in the oxide will
degrade oxide reliability. Therefore, a process that provides a more **uniform**
distribution of **nitrogen** in the silicon **oxynitride** layer is desired.

After the nitridation step, the wafer was subjected to an oxidation step at
1000.degree. C. for 45 seconds to form a layer of silicon oxynitride. As
illustrated in FIG. 5, the nitrogen is evenly distributed in the silicon
oxynitride layer after the oxidations step. The nitride distribution was
determined using medium energy ion scattering analysis. As noted above, it is
advantageous if the **nitrogen is uniformly** distributed in the silicon **oxynitride**
layer instead of concentrated at the interface between the

silicon **oxynitride**
layer and the underlying silicon. The advantage derives from the fact that
boron will not penetrate as far into a layer in which the nitrogen is evenly
distributed as it will into a layer in which the nitrogen is concentrated at
the interface. Consequently, boron does not concentrate at the interface
between the silicon oxynitride layer and the underlying silicon substrate and
is therefore less likely to diffuse into the underlying silicon.

US-PAT-NO: 6252296

DOCUMENT-IDENTIFIER: US 6252296 B1

TITLE: Semiconductor device with silicon oxynitride gate insulating film

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According to the invention, the gas including non-pyrolized N.sub.2 O is brought into contact with the surface of the heated silicon substrate. It was found out that nitrogen in the silicon oxynitride film formed by this method localizes at an interface between the silicon substrate and the silicon oxynitride film. It was also found out that an Si--NO.sub.2 chemical bond unit does not exist at the interface and a portion other than the interface (hereinafter, referred to as a bulk portion). It was also made clear that the silicon **oxynitride** film having **nitrogen** localized at the interface has TDDB characteristics improved compared with a silicon **oxynitride** film having **nitrogen uniformly** distributed in the film.

DOCUMENT-IDENTIFIER: US 20010011725 A1

TITLE: Semiconductor device and method of producing the same

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[0015] In order to solve the above-mentioned problems according to the present invention, a silicon **oxynitride** film is formed by a plasma CVD method by using SiH.sub.4, **N.sub.2O and H.sub.2,** and this film is used as a base film for a TFT. The properties of the silicon **oxynitride** film that is formed is controlled by, chiefly, varying the flow rates of **N.sub.2O and H.sub.2**. The hydrogen concentration and the nitrogen concentration are increased in the film upon increasing the flow rate of H.sub.2. Upon increasing the flow rate of N.sub.2O, further, the hydrogen concentration and the nitrogen concentration decrease in the film, and the oxygen concentration increases. On the other hand, the silicon concentration does not almost change even if only a ratio of N.sub.2 and N.sub.2O gas flows is changed. This makes it possible to form a silicon oxynitride film on the side of the substrate, the silicon oxynitride film having a composition exhibiting properties which are merits of the silicon nitride film, and to form a silicon oxynitride film on the side of the active layer, the silicon oxynitride film having a composition exhibiting properties which are merits of the silicon oxide film, while continuously changing the compositions thereof, thereby to form a base film of good quality picking up merits of both the silicon nitride film and the silicon oxide film. The silicon oxynitride films exhibiting the above-mentioned

properties are formed by the same film-forming method by simply changing the gas flow rate ratios, and can be formed in the same film-forming chamber contributing to enhancing the productivity.

[0016] Concretely speaking, there are formed a silicon **oxynitride** film formed over SiH.sub.4, **N.sub.2O and H.sub.2** flow rate ratios of Xh=0.5 to 5 (Xh=H.sub.2/(SiH.sub.4+N.sub.2O)), Xg=0.94 to 0.97 (Xg=N.sub.2O/(SiH.sub.4+N.sub.2O)), and a silicon **oxynitride** film formed over flow rate ratios of Xh=0 (Xh=H.sub.2/(SiH.sub.4+N.sub.2O)), Xg=0.97 to 0.99 (Xg=N.sub.2O/(SiH.sub.4+N.sub.2O)). these silicon oxynitride films being separately used.

[0021] The silicon oxynitride film is formed by using a plasma device which is constituted by parallel flat plates of the capacitor-coupled type. It is also allowable to use the one of the induction coupled type or a plasma CVD device utilizing the energy of magnetic field such as of electron cyclotron resonance. The composition of the silicon **oxynitride** film is varied by using SiH.sub.4 and **N.sub.2O gases and by adding H.sub.2** thereto. The plasma is formed under a pressure of 10 Pa to 133 Pa (desirably, 20 Pa to 40 Pa), with a high-frequency power density of 0.2 W/cm.sup.2 to 1 W/cm.sup.2 (preferably, 0.3 W/cm.sup.2 to 0.5 W/cm.sup.2), at a substrate temperature of 200.degree. C. to 450.degree. C. (preferably, 300.degree. C. to 400.degree. C.), and an oscillation frequency of high-frequency power source of 10 MHz to 120 MHz (preferably, 27 MHz to 60 MHz).

[0022] Table 1 shows three kinds of preparation conditions. The condition #210 is for forming the silicon oxynitride film from SiH.sub.4 and N.sub.2O. The

conditions #211 and #212 are when H_2 is added to SiH_4 and N_2O, and in which the flow rate of H_2 being added is varied. In this specification, the silicon **oxynitride** film formed from SiH_4 and N_2O is expressed as silicon **oxynitride** film (A), and the silicon **oxynitride** film formed from SiH_4, **N_2O and H_2** is expressed as silicon **oxynitride** film (B). The silicon **oxynitride** film (A) is formed with SiH_4, **N_2O and H_2** flow rate ratios of $Xh=0$ ($Xh=H_2/(SiH_4+N_2O)$) and $Xg=0.97$ to 0.99 ($Xg=N_2O/(SiH_4+N_2O)$), and the silicon **oxynitride** film (B) is formed with SiH_4, **N_2O and H_2** flow rate ratios of $Xh=0.5$ to 5 ($Xh=H_2/(SiH_4+N_2O)$) and $Xg=0.94$ to 0.97 ($Xg=N_2O/(SiH_4+N_2O)$).

[0054] The reaction chamber consists of only one chamber but the silicon **oxynitride** films (A) and (B) can be continuously formed in the same reaction chamber by controlling the feeding amounts of SiH_4, **N_2O, H_2** and by controlling the high-frequency electric power and the reaction pressure. When the substrate has a large size, rather, the floor area for installation can be decreased making it possible to save space.

[0057] The silicon **oxynitride** films (A) and (B) can be continuously formed in the same reaction chamber since the SiH_4, **N_2O and H_2** feeding rates, high-frequency electric power and reaction pressure can be controlled, and may assume the two-layer structure as described above, or the composition thereof may be continuously changed by changing the rate of feeding the gases with the passage of film-forming time. In any way, the apparatus of the constitution shown in FIG. 2B contributes to enhancing the

productivity.

[0063] Then, as shown in FIG. 3, a base film 302 is formed as a blocking layer to prevent contamination with alkali metal elements and other impurities from the substrate 301. Under the forming conditions shown in Table 1, the interface with the substrate is formed of a silicon **oxynitride** film (B), and the composition is continuously varied into a composition of the silicon **oxynitride** film (A) by controlling the flow rates of SiH.sub.4, **N.sub.2O and H.sub.2** by using a mass flow controller. The silicon oxynitride film (B) containing nitrogen in large amounts is formed on the side of the substrate to prevent the diffusion if impurities into the active layer from the substrate, and the silicon oxynitride film (A) containing nitrogen in small amounts is formed on the side of the active layer to maintain a favorable interfacial state relative to the active layer. A dotted line in FIG. 3 represents a portion where the composition just assumes an intermediate value. This portion may be at the center in the thickness of the film, or may be closer to the semiconductor layer or to the substrate. Concretely speaking, formation of the film is commenced by, first, feeding SiH.sub.4 at a rate of 5 SCCM, N.sub.2O at a rate of 120 SCCM and H.sub.2 at a rate of 125 SCCM, setting Xg=0.96 at Xh=1, controlling the pressure to be 20 Pa, and supplying a high-frequency electric power of 27 MHz 0.4 mW/cm.sup.2. Then, by taking the film-forming rate into consideration, the flow rate of N.sub.2O is increased up to 500 SCCM at a moment when the film formation is finished, the flow rate of H.sub.2 is decreased to be 0 SCCM, and Xg is set to be 0.99 at Xh=0. The flow rate of SiH.sub.4 is controlled from 5 SCCM to 4 SCCM, i.e., changed over at the

portion of the dotted line in FIG. 3. The base film is thus formed maintaining a thickness of 150 nm. The thickness of the base film is in no way limited thereto only but may assume a thickness of 50 nm to 300 nm (preferably, from 80 nm to 150 nm), and the silicon oxynitride films (A) and (B) may be laminated as described above. The film-forming conditions shown here are only examples, and no limitation is imposed thereon provided the compositions shown in Table 2 are obtained.

[0089] After the steps up to FIG. 5C have finished, a first interlayer insulating film 155 is formed on the gate electrodes and on the gate-insulating films. The first interlayer insulating film may be formed of a silicon oxide film, a silicon oxynitride film, a silicon nitride film, or a laminated-layer film of a combination thereof. In any way, the first interlayer insulating film 155 is formed of an inorganic insulating material. The first interlayer insulating film 155 has a thickness of 100 nm to 200 nm. Here, when the silicon oxide film is used, the film is formed by the plasma CVD method by mixing TEOS and O.sub.2 together, under a reaction pressure of 40 Pa maintaining the substrate at a temperature of 300.degree. C. to 400.degree. C. and by generating an electric discharge with a high-frequency (13.56 MHz) power density of 0.5 W/cm.sup.2 to 0.8 W/cm.sup.2. When the silicon oxynitride film is to be used, further, the film may be the silicon oxynitride film formed of SiH.sub.4, N.sub.2O and NH.sub.3 by the plasma CVD method or may be the silicon oxynitride film formed of SiH.sub.4 and N.sub.2O. The forming conditions in this case are a reaction pressure of 20 Pa to 200 Pa, a substrate temperature of 300.degree. C. to 400.degree. C., and a high-frequency (60

MHz) power density of 0.1 W/cm.sup.2 to 1.0 W/cm.sup.2. Or, there may be used a hydrogenated silicon **oxynitride** film formed of SiH.sub.4, **N.sub.2O and H.sub.2**. The silicon nitride film can similarly be formed of SiH.sub.4 and NH.sub.3 by the plasma CVD method.

[0141] According to this invention, the silicon **oxynitride** film is formed by the plasma CVD method by using SiH.sub.4, **N.sub.2O and H.sub.2** as starting material gases and varying the flow rate ratios of the starting material gases. Thus, there is formed a favorable base film in which the composition of N, O and H is continuously varied. When used as the base film, the film of the invention not only prevents the diffusion of impurities from the substrate owing to its blocking effect but also forms a favorable interface relative to the active layer to prevent deterioration in the TFT characteristics. Since the film is formed in the same chamber, the treatment time is shortened, the TFT characteristics are stabilized and the productivity is enhanced.

22. A method of producing a semiconductor device comprising the steps of: forming an insulating film on a substrate; and forming a semiconductor film on said insulating film, wherein said insulating film comprises silicon **oxynitride** film formed from SiH.sub.4, **N.sub.2O, and H.sub.2,** and wherein said silicon **oxynitride** film is formed by decreasing a flow rate of said H.sub.2 and increasing a flow rate of said N.sub.2O from a region in contact with said substrate to a region in contact with said semiconductor film.